



# Functionalizing carbon nitride with heavy atom-free spin converters for enhanced $^1\text{O}_2$ generation



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## ABSTRACT

Carbon nitride as a metal-free conjugated polymer exhibits an intriguing prospect for the design of advanced photosensitizers for singlet oxygen ( $^1\text{O}_2$ ) generation. However, the intersystem crossing (ISC) process is quite insufficient in carbon nitride, limiting the  $^1\text{O}_2$  generation. Here, we report a facile and general strategy to confined benzophenone as a heavy atom-free spin converter dopant in carbon nitride via the facile copolymerization. With proper energy level matching between the heavy atom-free spin converter and various ligands based on carbon nitride precursors, the proper combination can decrease the singlet-triplet energy gap ( $\Delta E_{\text{ST}}$ ) and hence generate  $^1\text{O}_2$  effectively. Due to its significant and selectivity for  $^1\text{O}_2$  generation, the as-prepared carbon nitride-based photosensitizer shows a high selective photooxidation activity for 1,5-dihydroxy-naphthalene (1,5-DHN). The product yield reached 71.8% after irradiation for 60 min, which was higher than that of cyclometalated  $\text{Pt}^{\text{II}}$  complexes (53.6%) in homogeneous photooxidation. This study can broaden the application of carbon nitride in the field of selective heterogeneous photooxidation due to simple operation, low cost, and high efficiency, making it a strong candidate for future industrialization.

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## 1. Introduction

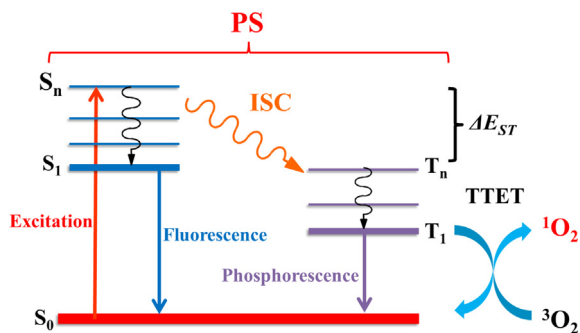
Singlet oxygen ( $^1\text{O}_2$ ) has proven to be an effective oxygen species for many selective organic syntheses, such as selective oxidation of primary alcohols to aldehydes [1] and conversion of anthracene derivatives to anthraquinone [2]. As a result, there is a need to efficiently create  $^1\text{O}_2$  for these and other reactions, beginning with the  $^3\text{O}_2$  ground state. One route is through the use of  $^1\text{O}_2$  photosensitizers that improve photon absorption and also demonstrate efficient intersystem crossing (ISC) [3]. As shown in Scheme 1,  $^1\text{O}_2$  photosensitizers work by first undergoing photoexcitation into a singlet excited state. These photosensitizers then undergo the crucial ISC process, so that the triplet state can sensitize oxygen through triplet-triplet energy transfer (TTET) [3–5]. Therefore, an efficient ISC process is the crucial factor for enhancing  $^1\text{O}_2$  generation. Previously, heavy atoms, such as Pt(II) [6,7], Ru(II) [8], I and Br [9,10], were used as spin converters to induce the ISC process. Unfortunately, it is limited by high cost, low quantum yield, easy

photobleaching and nonrecyclability. Recently, metal-free conjugated polymers based on carbon nitride exhibited an intriguing prospect for photooxidation [11–13]. However, there remain few rational design strategies for these conjugated polymers to selectively enhance  $^1\text{O}_2$  generation.

Incorporation of functional groups with carbon nitride that undergo efficient ISC, otherwise known as heavy atom-free spin converters, is a facile and inexpensive way to selectively enhance  $^1\text{O}_2$  generation [14,15]. For example, benzophenone with a low-lying  $n-\pi^*$  transition is a good candidate for the spin converter due to large spin-orbit coupling, and its ISC efficiency can reach 100% [16,17]. However, chemical modification with ligands often induces an unpredictable change of photochemical properties, such as alteration of the singlet-triplet energy gap ( $\Delta E_{\text{ST}}$ ) [18,19]. It is known that a smaller  $\Delta E_{\text{ST}}$  generally produces a more efficient ISC process and  $^1\text{O}_2$  generation (Scheme 1) [20,21]. If the ligand unit, the moiety connected to the spin converter, has extremely large  $\pi$  conjugation, the low-lying transition would be  $\pi-\pi^*$  instead of  $n-\pi^*$ . This would increase  $\Delta E_{\text{ST}}$  and prohibit the ISC process [22]. On the other hand, a ligand structure with less  $\pi$  conjugation could also influence  $\Delta E_{\text{ST}}$ . Therefore, the proper ligand plays a very important role for the ISC process and  $^1\text{O}_2$  generation.

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**Scheme 1.** The modified Jablonski diagram of the photoexcitation energy transfer process of a photosensitizer (PS) that undergoes efficient intersystem crossing (ISC) to enable triplet–triplet energy transfer (TTET) to generate singlet oxygen ( $^1\text{O}_2$ ). The functionalization of PS with compounds that undergo ISC (spin converters) is one approach to producing  $^1\text{O}_2$ . The smaller singlet–triplet energy gap ( $\Delta E_{ST}$ ) benefits efficient ISC process and  $^1\text{O}_2$  generation.

Based on this principle, we used precursors of carbon nitride (melamine and melem) as ligands of heavy atom-free spin converters (benzophenone) to explore their structure–property relationship for enhancing  $^1\text{O}_2$  generation. The heavy atom-free spin converter doped carbon nitride was prepared via the facile copolymerization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (it has the benzophenone structure to function as the spin converter) and a carbon nitride precursor. The structures were confirmed by TEM, SEM, solid-state  $^{13}\text{C}$  NMR, XPS and XRD. The modified carbon nitride is shown to greatly enhance  $^1\text{O}_2$  generation and selective photooxidation of 1,5-dihydroxynaphthalene (1,5-DHN). 1,5-DHN is a substance that contaminates water, but its product (5-hydroxy-1,4-naphthalenedione, Juglone) obtained after oxidation has hemostatic and antibacterial activity. Furthermore, ESR, steady state/time-resolved luminescence spectroscopy and DFT calculations were used to explore the structure–property relationship for enhancing  $^1\text{O}_2$  generation. This work provides a basis for broadening the application of carbon nitride in the field of selective photooxidation due to simple operation, low cost and high efficiency. More importantly, the heterogeneous photocatalysis process enables the product to be easily obtained by simple filtration, which is beneficial for industrial applications.

## 2. Experimental

### 2.1. Materials preparation

3,3',4,4'-benzophenonetetra-carboxylic dianhydride (BTDA), 3,3,4,4'-biphenyltetracarboxylic dianhydride (BPDA) and melamine were obtained from Aladdin Industrial Corporation. All the chemicals in our experiment were directly used without further purification.

Melem was synthesized by heating melamine placed in a porcelain crucible with a cover at  $425\text{ }^\circ\text{C}$  for 4 h in a muffle furnace [23]. Similarly, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) was synthesized by heating melamine at  $550\text{ }^\circ\text{C}$  for 4 h in a muffle furnace [24].

Photocatalysts based on carbon nitride were synthesized by facile thermal condensation of melem and BTDA. In detail, 1 g of powder mixture of melem and BTDA (the molar ratios of melem and BTDA were 5:1, 3:1, 1:1, 1:3, 1:5, respectively) was put into a railboat and heated at  $5\text{ }^\circ\text{C}/\text{min}$  up to  $300\text{ }^\circ\text{C}$  for 4 h under the protection of  $\text{N}_2$ . The samples (the molar ratio of melem and BTDA at 1:1) were calcined under different temperature. The optimum temperature was chosen at  $300\text{ }^\circ\text{C}$  (Table S1). In order to avoid the influence of unreacted BTDA, the resultant block solid was treated with ultrasound and washed with N,N-dimethylformamide

(DMF) three times. Finally, the light brown product denoted as CN-T was filtered and dried at  $60\text{ }^\circ\text{C}$ . Similarly, other control samples of CN-P (melem and BPDA without benzophenone structure were mixed at the ratio of 1:1) and ME-T (melamine and BTDA were mixed at the ratio of 1:1) were prepared using the same method.

### 2.2. Materials characterization

The morphologies of the samples were characterized by scanning electron microscopy (SEM) (Hitachi S-4800, Japan) and transmission electron microscopy (TEM) (JEM-2100UHR, Japan). XRD patterns were obtained on a powder X-ray diffractometer at 40 kV and 15 mA using Cu K $\alpha$  radiation (X'Pert PRO MPD, Holland). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer equipped with a pre-reduction chamber. Solid-state  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$  NMR) was measured on a Bruker Advance III 400 M spectrometer equipped with a 9.4 T magnet. The UV–Vis spectra were recorded on a UV–Vis spectrophotometer (UV-2700, Shimadzu, Japan). The  $^1\text{O}_2$  emission signal of the CN-T photosensitizer was detected in a fluorescence spectrometer FLS980 (Edinburgh Instruments Ltd.) with a 450 W Xe lamp and a NIR detector. The sample was excited at 360 nm. The experimental conditions were excitation and emission bandwidths of 15 nm, integration time 2 s/step (0.1 s dwell time  $\times$  20 repeats) and step of 1 nm for the sample. The ns-domain time-resolved fluorescence spectra and the  $\mu\text{s}$ -domain time-resolved spectra were also obtained on an FLS980 fluorescence spectrometer (Edinburgh Instruments Ltd.). Triplet emission spectra and lifetimes were also characterized with a Horiba Jobin-Yvon fluorolog spectrometer system.

### 2.3. Photooxidation 1,5-DHN test

The photochemical reaction was performed at room temperature under air atmosphere in a round bottom flask (50 mL) with irradiation by a 35 W xenon lamp ( $600\text{ W}/\text{m}^2$ ). The MeCN/ $\text{H}_2\text{O}$  ( $v/v = 5:1$ ) mixed aqueous solution (20 mL) containing  $1.0 \times 10^{-4}$  mol/L of 1,5-DHN and photocatalysts (20.0 mg) was irradiated at  $\lambda > 385\text{ nm}$  (the light with a wavelength shorter than 385 nm was blocked by 0.72 M  $\text{NaNO}_2$  solution). UV–Vis absorption spectra were used to record at intervals of 10 min. The consumption of 1,5-DHN was monitored by a decrease in the absorption at 331 nm, and the concentration of 1,5-DHN was calculated by using its molar extinction coefficient ( $\epsilon = 7664\text{ M}^{-1}\text{ cm}^{-1}$ ). Juglone production at intervals of 10 min was monitored by an increase in the absorption peak at 419 nm. The concentration of Juglone was also calculated by using its molar extinction coefficient ( $\epsilon = 3567\text{ M}^{-1}\text{ cm}^{-1}$ ), and the yield of Juglone was calculated according to the following eqn:

$$\text{Yield} = \frac{100 \times A_i(\text{Juglone})/\epsilon(\text{Juglone})}{C_{\text{initial}}(1,5\text{-DHN})} \times 100\%$$

$A_i(\text{Juglone})$  is the absorbance of Juglone in solution;  $\epsilon(\text{Juglone})$  is the molar extinction coefficient of Juglone;  $C_{\text{initial}}(1,5\text{-DHN})$  is the initial concentration of 1,5-DHN.

### 2.4. Electron spin resonance (ESR) spectroscopy

Electron spin resonance (ESR) spectra were recorded at room temperature using a JEOL JES FA200 spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis in the dark and illuminated directly in the cavity of the ESR spectrometer. In the whole test process, 2,2,6,6-tetramethylpiperidine

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